

The Contact Angle between Liquid Iron and a Single Crystal, Alumina Substrate at 1873 K: Effects of Oxygen and Droplet Size

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The contact angle for iron on a single-crystal alumina substrate varied from 40 to 120 deg by changing the gas atmosphere and droplet size. At constant droplet size, the contact angle was a strong function of the partial pressure of oxygen and increased as oxygen partial pressure decreased. However, at oxygen partial pressures less than 10^{-18} atm, the contact angle markedly decreased as a zone of reactive wetting was reached due to interaction between alumina and the droplet. The effect of droplet size on the contact angle between liquid iron and a single-crystal alumina substrate was measured at constant oxygen activity and temperature. In an argon-hydrogen atmosphere where oxygen activity was constant, the contact angle increased with increasing droplet size and varied from 40 to 80 deg as the droplet radius increased from 1.5 to 4 mm. A similar though smaller effect was measured in CO atmospheres that were in equilibrium with carbon. In this case, the contact angle ranged from 105 to 118 deg as droplet size increased. Experiments in CO/CO₂ atmospheres showed little effect of droplet size at oxygen partial pressures less than 5×10^{-12} atm, but indicated a significant effect at oxygen partial pressures greater than 10^{-11} atm.

I. INTRODUCTION

MANY researchers have studied the wetting phenomena between molten iron and solid oxides.^[1-11] The effect of oxygen on the interfacial phenomena has been documented by a number of experimentalists using the sessile drop technique where surface tension decreased with increasing oxygen content.^[4,5] The contact angle behavior as a function of oxygen content is less well understood and some investigators have shown a maximum value at very low oxygen contents.^[5] The wetting phenomena of iron on Al₂O₃ was reviewed by Nogi.^[10] Previous measurements of the contact angle of iron on various oxides are difficult to reconcile due to the large variation between the results of different investigators that may be related to atmospheric differences, impurity content, roughness, and experimental technique. Thus, in this study, the contact angle was measured with a high-purity (single-crystal alumina) substrate, a high-purity iron, with controlled substrate roughness, and as a function of the partial pressure of oxygen in the gas phase.

Most interfacial properties of liquid steel on solid oxides have been investigated by the sessile drop technique. By determining the contact angle (θ) and the interfacial energy between liquid-gas interface ($\gamma_{\text{liquid-gas}}$), the interfacial energies

between solid-gas ($\gamma_{\text{solid-gas}}$) and solid-liquid ($\gamma_{\text{liquid-solid}}$) are commonly related by Young's relation:

$$\gamma_{\text{solid-gas}} - \gamma_{\text{liquid-solid}} = \gamma_{\text{liquid-gas}} \cdot \cos \theta \quad [1]$$

However, it was first postulated by Gibbs^[12] that various sizes of droplets would exhibit different contact angles if the three-phase line contact energy was significant. The length and curvature of three-phase contact line varies with the changing radius of contact area of the droplet, *i.e.*, droplet size. Therefore, the line energy and its effect on the equilibrium shape of a droplet should vary with the droplet contact radius and become more important as the droplet size decreases.

If one includes the line energy in the minimization of the free energy of an equilibrium three-dimensional droplet, the following relationship is found:^[12]

$$\gamma_{\text{solid-gas}} - \gamma_{\text{liquid-solid}} = \gamma_{\text{liquid-gas}} \cdot \cos \theta + \frac{\kappa}{R} \quad [2]$$

where κ and R are the line energy and the radius of contact area. Of course, this relation becomes Young's relation at large values of R and low values of $\tilde{\kappa}$.

In this study, measurements were made to determine if there was an effect of droplet size on the contact angle and if Eq. [2] could be used to determine the value of the line energy for a pure iron droplet on single-crystal Al₂O₃ substrates in Ar/5 pct H₂, C/CO, and CO/CO₂ gas atmospheres.

II. EXPERIMENTAL DETAILS

The sessile drop technique was used in the present study to determine the contact angle as a function of the droplet size. Details of the technique were published earlier^[1-11] and specific details^[11] related to these experiments are documented in Sections A through C.

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A. Experimental Apparatus

A horizontal resistance furnace with MoSi₂ heater with an Al₂O₃ reaction tube (3 in. in diameter and 42 in. in length) was placed in horizontal position and sealed. Two Pt-Rh6 pct/Pt-Rh30 pct thermocouples were placed inside the tube. One was placed in the vicinity of the specimen while the other was placed on the tube.

B. Atmosphere

Ultra-high-purity argon gas, an Ar/5 pct H₂ mixture, CO, and CO/CO₂ gas mixtures were used as carrier gases. Argon was purified by flowing the gas overheated Cu and Mg turnings. Sponge titanium or graphite was also set inside the furnace in the argon or CO atmosphere experiments, respectively. Under experimental conditions, the titanium and graphite were controlled at 1673 and 1873 K, respectively. The CO/CO₂ was mixed to form oxygen partial pressures from 2.1×10^{-13} to 2.1×10^{-11} atm.

C. Metal and Substrate Composition

To eliminate issues of alumina substrate purity, single-crystal alumina substrate materials were purchased from Alfa Aesar (Reagent grade 99.9 pct Al₂O₃), because polycrystalline alumina samples were found to be quite variable in quality. The surface roughness, *Ra*, was measured as 0.02 μm of the single-crystal substrates. The iron samples were also purchased from Alfa Aesar and were of the following chemistry: 99.9985 pct Fe, which included measurable impurity contents of Cu 1 ppm, Mg 2 ppm, and Ti 2 ppm.

III. RESULTS AND DISCUSSION

A. Argon-Hydrogen and Carbon Monoxide Atmospheres

Figure 1 shows the relationship between the contact angle and the droplet radius for two experimental conditions: Ar-H₂ and CO. The contact angle varied with changing contact radius of the droplet in Ar/H₂ and was a strong function of the details of the gas atmosphere at a given droplet radius. In the argon-hydrogen gas atmosphere, where oxygen activity was set using titanium, the contact angle increased with increasing droplet size and varied from 40 to 80 deg as the droplet radius increased from 1.5 to 4 mm. A similar though smaller effect was measured in CO atmospheres that were equilibrated with carbon. In this case, the contact angle was a weak function of droplet size, increasing slightly from 105 to 118 deg as droplet size increased. Thus, the measured contact angle is a function of the details of the gas that is used and the size of the droplet.

In order to calculate the effect of line energy, the relationship between a contact angle and line energy can be rewritten from Eq. [2] as

$$\gamma_{\text{liquid-gas}} \cdot \cos \theta = (\gamma_{\text{solid-gas}} - \gamma_{\text{liquid-solid}}) - \kappa \cdot \frac{1}{R} \quad [3]$$

If the line energy is constant in a given gas atmosphere and $\gamma_{\text{liquid-gas}}$ is known, the relationship between the inverse

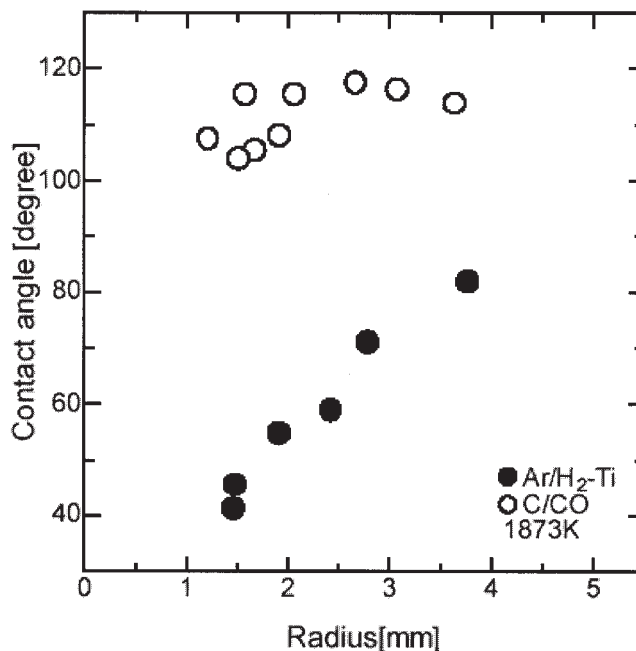


Fig. 1—Contact angle as a function of droplet radius for Ar-H₂ and CO gas mixtures.

of radius and cosine of contact angle would also be linear. The line energy can thus be obtained from the slope of the data without knowing the other interfacial energy values.

The surface tension of pure liquid iron as a function of temperature been reported by Kasama *et al.*^[1]

$$\gamma_{\text{liquid-gas}}^0 = 1918 - 0.43(T - 1811) \text{ [mN/m]} \quad [4]$$

Jimbo and Cramb^[2] obtained the effect of oxygen on the surface tension liquid iron at 1823 K as

$$\gamma_{\text{liquid-gas}} = \gamma_{\text{liquid-gas}}^0 - 279 \ln(1 + 140 \cdot a_o) \text{ [mN/m]} \quad [5]$$

The oxygen activity in liquid iron can be related to the partial pressure of oxygen in the gas phase using the following relations:

$$\frac{1}{2} \text{O}_2 = \text{Pct O} \quad [6]$$

$$\Delta G_6^0 = -117,110 - 3.39T \text{ [J/mol]}^{[13]} \quad [7]$$

According to Eq. [4], γ^0 is 1891 mN/m at 1873 K and the soluble oxygen decreases the surface tension according to Eq. [5]. The variation of surface tension should be very small in an Ar/H₂ atmosphere as the atmospheric oxygen is set by the kinetics of the reaction between titanium and oxygen. In the other gas atmospheres, the partial pressure of oxygen is set by the gas phase and the surface tension of liquid iron can be estimated at 1873 K as 1891 mN/m in Ar/H₂ and 1889 mN/m in C/CO atmospheres.

The relationships between the radius of the specimen and this function (Eq. [3]) are shown in Figures 2 and 3. In each figure, a correlation between the inverse of the radius and

contact angle is given and the contact angle at infinite radius calculated. The slopes show that the line energies are $-2450 \mu\text{N}$ in Ar/H_2 and $-590 \mu\text{N}$ in CO . These results indicate that line energies are negative due to the increase in wettability measured in these gas atmospheres as droplet size decreases.

When the radius of the specimen tends to infinity, the contact angle would be the value found where $1/R = 0$ in Figures 2 and 3. Therefore, the contact angle of an infinitely large droplet is shown at the intercept. The value of this

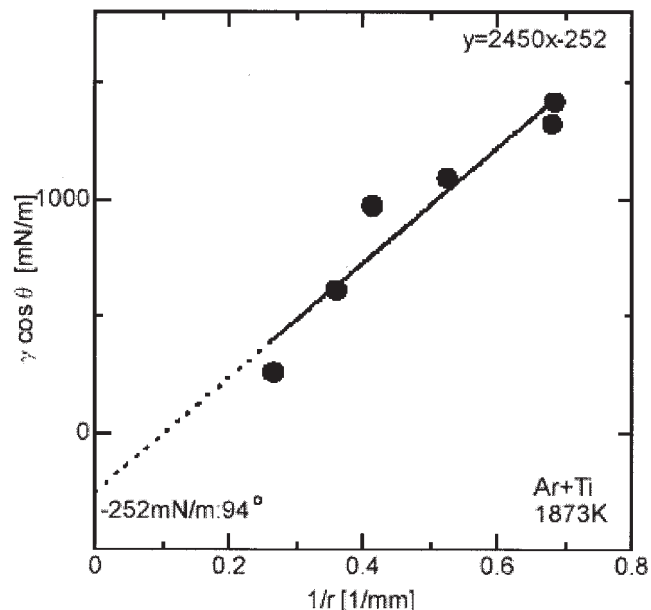


Fig. 2—Relationship between contact angle and reciprocal radius for Ar/H_2 gas mixtures (line tension and contact angle at infinite radius are also shown at intercept).

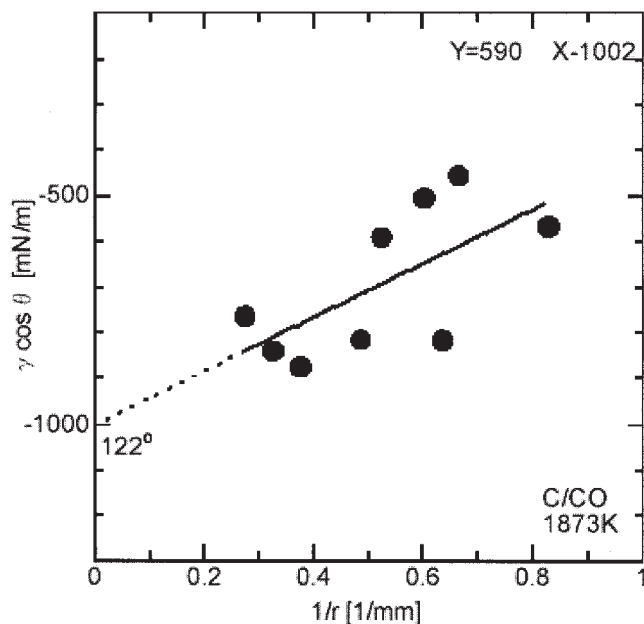


Fig. 3—Relationship between contact angle and reciprocal radius for CO in equilibrium with carbon (line tension and contact angle at infinite radius are also shown at intercept).

contact angle varies with changing gas atmosphere. The contact angle thus should be discussed in conjunction with the contact area of the droplet, if droplet size is important. The contact angle of an infinite radius drop should be used as a standard expression of contact angle measurement for comparison with other measurements. Table I shows the contact angle of infinite radius droplets and the measured line energies for different atmospheric conditions.

It is interesting to note that the change in the gas atmosphere changes the contact angle from wetting ($<90^\circ$) to nonwetting ($>90^\circ$). To account for this large variation in contact angles, one must postulate that one has gone from close to an equilibrium experiment (at high contact angle) to a nonequilibrium experiment (at low contact angle) where the droplet is reacting with the substrate and thus is exhibiting reactive wetting behavior.

Because of the oxidation of Ti in the Ar/H_2 experiments, the equilibrated oxygen partial pressure ideally will be less than 10^{-24} atm at 1673 K. However, in reality, such a pressure is not possible because the actual oxygen potential is determined by the kinetics of the reaction between titanium and oxygen and the evaporation of the substrate and the reaction tube (Al_2O_3) because this oxygen partial pressure is below the stability point for alumina at this temperature. The equilibrium condition in the droplet must ensure that the following equilibrium is met:



As the oxygen partial pressure is reduced in the system, alumina will dissociate. This is a potential mechanism that drives reactive wetting in a low oxygen content gas atmosphere. The iron droplet wets alumina in highly deoxidized Ar/H_2 atmospheres due to Reaction [8], and the droplet is difficult to remove from the substrate after the experiment; indicating that there is a reaction between the droplet and the substrate. The alumina that is not in contact with the droplet also changes surface morphology during these experiments. Both of these experimental observations suggest that the system is not in equilibrium and is in fact reacting.

The contact angle of pure Fe and $\text{Fe}-0.13$ pct Al alloy under Ar/H_2 atmosphere is shown in Figure 4 as a function of time. The droplet weight is 0.25 g. The contact angle of pure iron is less than that of $\text{Fe}-\text{Al}$ alloy within first 1000 seconds. Thus, the reaction between the substrate and the droplet is the driving energy that allows droplet spreading, and the large apparent line energy measured in Ar/H_2 atmosphere may be indicative of strong reactive wetting rather than a large true value for equilibrium line tension.

B. CO/CO_2 Gas Atmospheres

The effect of conducting the experiments in CO/CO_2 atmospheres is shown in Figure 5 as a function of droplet radius. Again, the contact angle is a function of the details of the gas atmosphere. Replotting these results according to Eq. [3] was done and is shown in Figures 6 through 9. At low oxygen partial pressures less than 4×10^{-12} atm, little effect of droplet size is seen. However, at higher oxygen partial pressures, the droplet size has an effect. The data on line tension is shown in Table I, as is the calculated infinite drop contact angle. In these experiments, extrapolation of the

droplet size data indicates that the contact angle varies only slightly with oxygen content but that the effect of droplet size under some conditions can be significant, while under others it is hardly significant.

If all of the data for line energy are plotted as a function of oxygen content (Figure 10), it appears that there is a maximum in line energy as a function of oxygen partial

pressure. This maximum is a result of the change from close to equilibrium conditions to nonequilibrium conditions. Thus, as oxygen decreases in the atmosphere, the line energy decreases until the point at which the substrate is no longer stable. At this point, reactive wetting begins and the apparent line energy increases. The maximum in the behavior of the line energy suggests that perhaps the effect of droplet

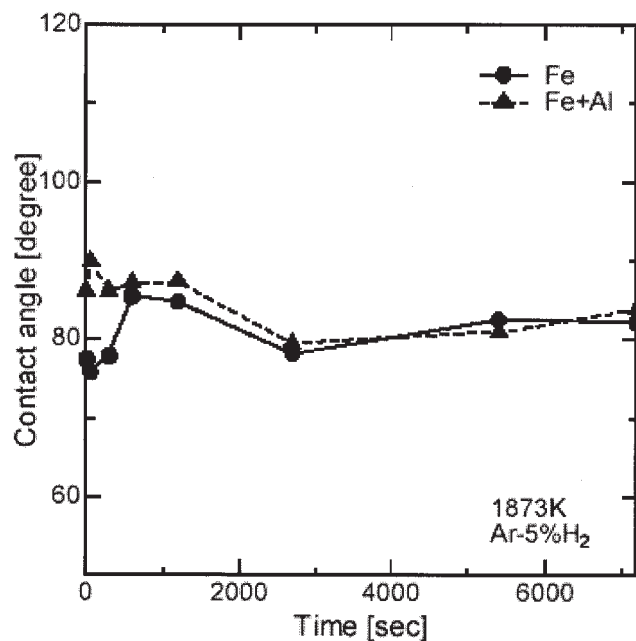


Fig. 4—Contact angle of pure iron and Fe-0.13 pct Al alloy as a function of time.

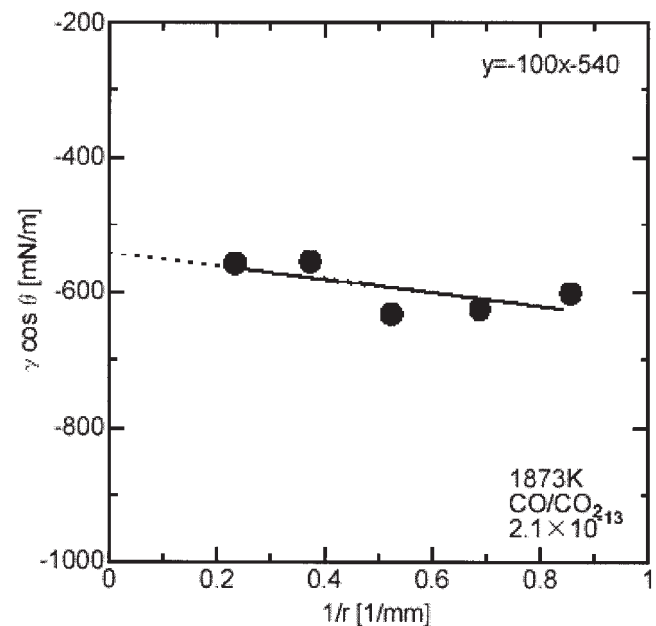


Fig. 6—Effect of radius on contact angle at an oxygen partial pressure of 2.1×10^{-13} atm.

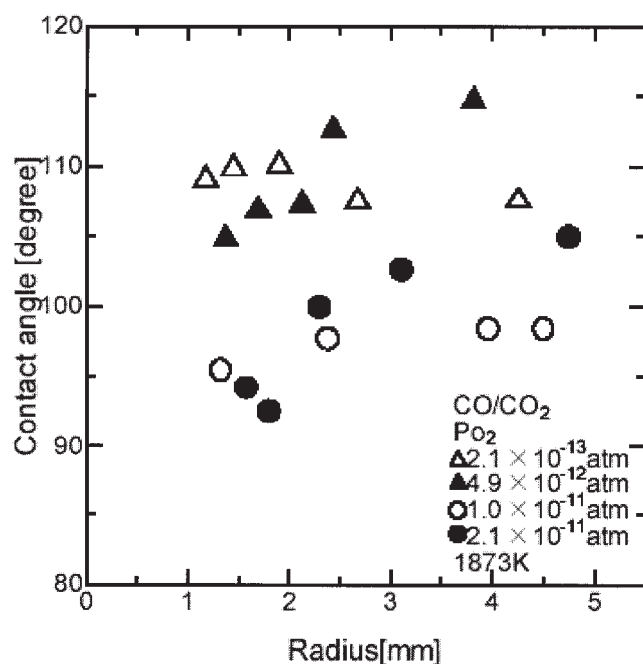


Fig. 5—Contact angle as a function of droplet radius in CO/CO₂ gas mixtures.

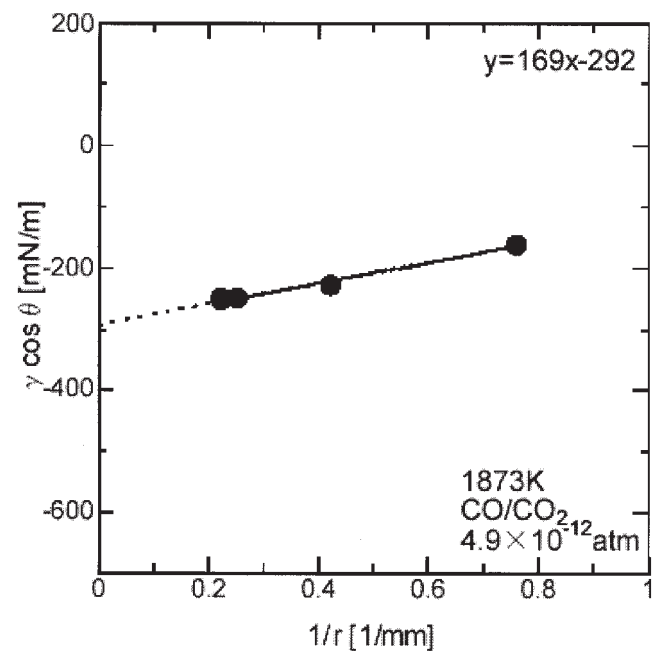


Fig. 7—Effect of radius on contact angle at an oxygen partial pressure of 4.9×10^{-12} atm.

size on contact is related to reaction rather than line energy. Thus, the minimum values of line energy determined by this approach are perhaps those closest to equilibrium conditions. For example, the decrease in line energy with increasing oxygen content could be indicative of another reaction such as compound formation between the droplet and the substrate.

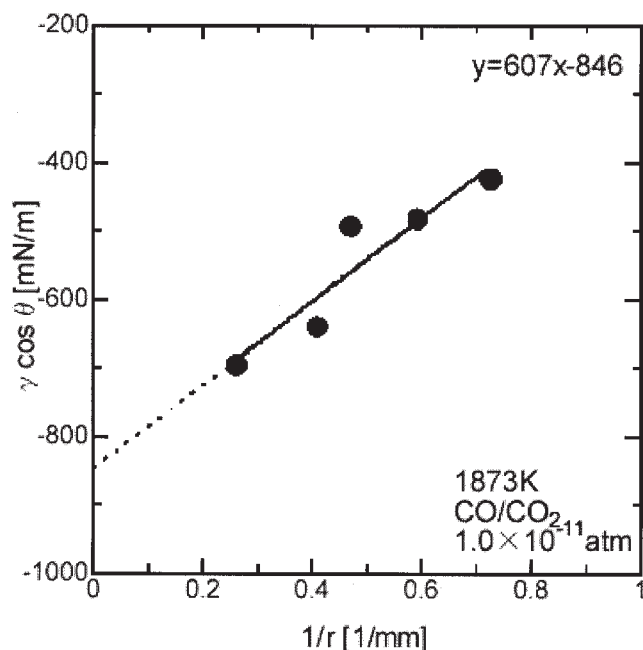


Fig. 8—Effect of radius on contact angle at an oxygen partial pressure of 1.0×10^{-11} atm.

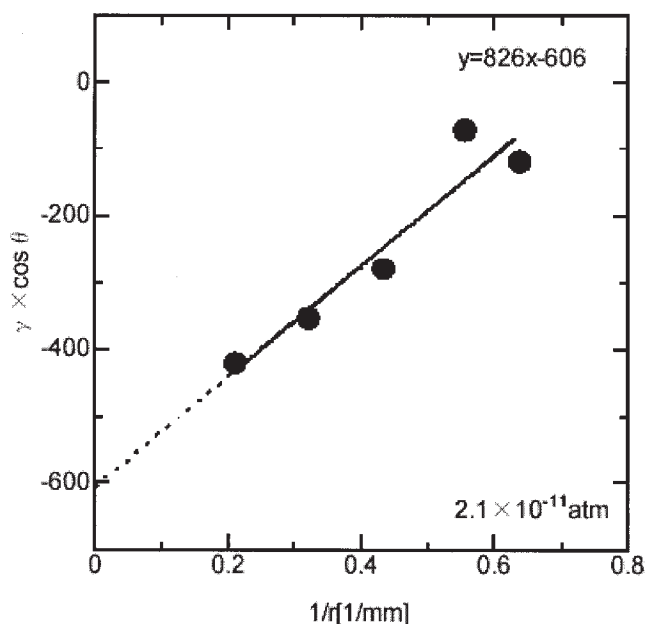


Fig. 9—Effect of radius on contact angle at an oxygen partial pressure of 2.1×10^{-11} atm.

C. The Effect of Oxygen Partial Pressure

During experiments with constant droplet size, the effects of oxygen content on the contact angle can be clearly documented (Figure [11]) for liquid iron droplets on single-crystal alumina, single-crystal Magnesia, and single-crystal magnesium aluminate spinel substrates. In Figure [11], the oxygen partial pressure was set by either the CO_2/CO ratio or by measurement of the oxygen partial pressure by an oxygen sensor. It can be seen that in all three substrates the contact angle is very sensitive to the details of the oxygen partial pressure in the gas phase. In a manner similar to that noted during the droplet size experiments, at very low oxygen partial pressures, the contact angle is wetting corresponding to reactive wetting with the substrate; however, in the area of the graph where

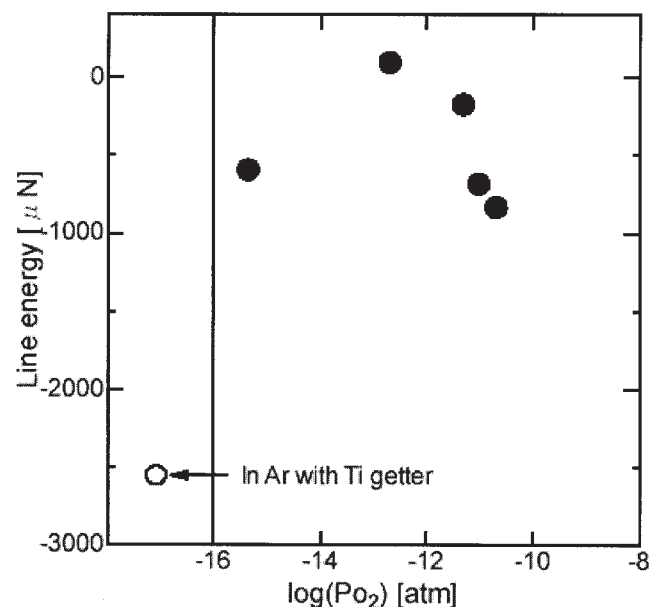


Fig. 10—Variation of line energy with partial pressure of oxygen.

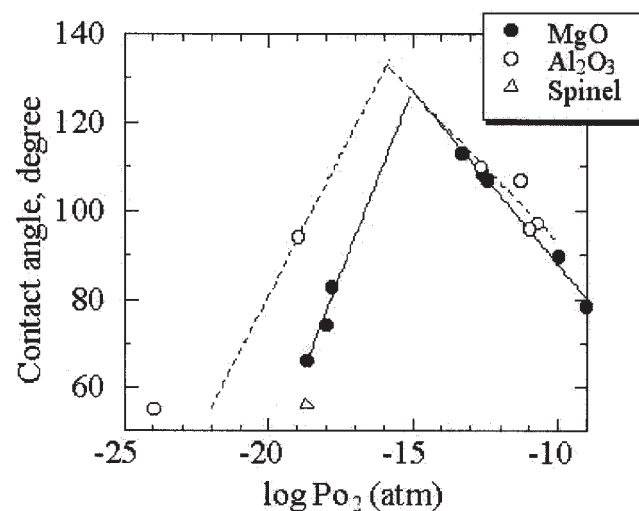


Fig. 11—Effect of gas phase oxygen content on the contact angle of liquid iron on alumina, magnesia, and magnesium aluminate (spinel) at 1873 K.

the substrate is stable, the contact angle is nonwetting and decreases with increasing oxygen partial pressure in the gas phase.

IV. CONCLUSIONS

Contact angles were measured to be a function of droplet size and the oxygen partial pressure of the gas atmosphere. These effects can cause large changes in the wetting behavior between liquid iron and alumina. Depending upon the details of an experiment, the contact angle can vary from 40 to 130 deg. Great care must be taken to accurately document experimental conditions, if one is to understand contact angle behavior in this high-temperature system.

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REFERENCES

1. A. Kasama, A. McLean, W. Amiller, Z. Morita, and M.J. Ward: *Can. Met. Q.*, 1983, vol. 22, p. 9.
2. I. Jimbo and A.W. Cramb: *Iron Steel Inst. Jpn. Int.*, 1992, vol. 32, pp. 26-35.
3. A.W. Cramb and I. Jimbo: *Steel Res.*, 1989, vol. 60, pp. 157-65.
4. N. Takiuchi, T. Taniguchi, Y. Tanaka, N. Shinozaki, and K. Mukai: *J. Jpn. Inst. Met.*, 1991, vol. 55, pp. 180-85.
5. K. Ogino, K. Nogi, and Y. Koshida: *Tetsu-to-Hagane*, 1973, vol. 59, pp. 1380-87.
6. K. Nakashima, K. Takihiro, K. Mori, and N. Shinozaki: *J. Jpn. Inst. Met.*, 1991, vol. 55, pp. 1199-1206.
7. K. Nogi and K. Ogino: *Can. Metall. Q.*, 1983, vol. 22, pp. 19-28.
8. N. Takiuchi, T. Taniguchi, N. Shinozaki, and K. Mukai: *J. Jpn. Inst. Met.*, 1991, vol. 55, pp. 44-49.
9. *Wettability at High Temperatures*, N. Eustatopoulos, M.G. Nicholas, and B. Drevet, eds., Pergamon Press, Elmsford, NJ, 1999.
10. K. Nogi: *Tetsu-to-Hagane*, 1998, vol. 84, pp. 1-6.
11. S. Ueda, H. Shi, and A.W. Cramb: *M. Wolf Symp.*, Apr., 2003, ISSTech, pp. 665-79.
12. J. Willard Gibbs: *Collected Works*, Vol. 1, *Thermodynamics*, Longmans-Green New York, NY, 1928.
13. D. Kashchiev: *Nucleation*, Butterworth Heinemann, London, 2000, Ch. 19.
14. *Steelmaking Data Source-Book*, JSPS 19th Committee, Gordon and Breach Science Publishers, New York, NY, 1988.